

What is claimed is:

1 1. A method of recycling a photoresist developer
2 solution containing tetra-methyl-ammonia hydroxide
3 (TMAH), comprising:
4 selecting m wavelengths between 220 nm and 250 nm,
5 wherein m is equal to or larger than 2;
6 measuring absorption values Y1 to Ym of the recycled
7 developer solution at the m wavelengths
8 respectively and an absorption value A1 at
9 wavelength 210 nm;
10 inputting the Y1 to Ym to an nth-degree polynomial,
11 $Y=C_1X^n+\dots+C_{n-1}X+C_n$, to generate a wavelength-
12 absorption relationship, wherein X is
13 wavelength, n is a positive integer, and C₁ to
14 C_n are coefficients of the relation;
15 inputting wavelength 210 nm into the wavelength-
16 absorption relationship to generate an
17 absorption value Y₂₁₀;
18 calculating a difference A3 between the A1 and Y₂₁₀
19 as the absorption value of TMAH in the
20 developer solution;
21 inputting A3 to an absorption calibration curve of
22 TMAH at 210 nm to generate a corresponding TMAH
23 concentration; and
24 adding TMAH into the recycled developer solution
25 according to the corresponding TMAH
26 concentration for reuse.

1 2. The method as claimed in claim 1, wherein the m
2 wavelengths are selected with an interval of 5 nm or 10
3 nm.

1 3. The method as claimed in claim 2, wherein the m
2 wavelengths are the 7 wavelengths 220 nm, 225 nm, 230 nm,
3 235 nm, 240 nm, 245 nm and 250 nm.

1 4. The method as claimed in claim 1, wherein the
2 nth-degree polynomial is a 2nd- to 5th-degree polynomial.

1 5. The method as claimed in claim 4, wherein the
2 nth-degree polynomial is a 3rd-degree polynomial as in
3 $Y=C_1X^3+C_2X^2+C_3X+C_4$.

1 6. The method as claimed in claim 1, further
2 comprising the steps of:

3 diluting the recycled developer solution when the
4 absorption value A1 at the wavelength 210 nm
5 exceeds 1.2;

6 re-measuring absorptions of the diluted recycled
7 developer solution at the m wavelength and 210
8 nm as Y1 to Ym and A1.

1 7. A method for recycling a photoresist developer
2 solution containing tetra-methyl-ammonia hydroxide
3 (TMAH), comprising:

4 measuring absorption values A1 and A2 of the
5 recycled developer solution at wavelength 210
6 nm and 220nm;

7 calculating an absorption value A3 of TMAH in the
8 developer solution by $A3 = A1 - A2 \times Co$, wherein Co

9 $= (A1' - A3') / A2'$, $A1'$ and $A2'$ are absorption
10 values of a recycled developer solution with
11 known TMAH concentration at wavelengths 210 nm
12 and 220 nm respectively, and $A3'$ is the
13 standard absorption value of the known TMAH
14 concentration at 210 nm;

15 inputting $A3$ to an absorption calibration curve of
16 TMAH at 210 nm to generate a corresponding TMAH
17 concentration; and

18 adding TMAH into the recycled developer solution
19 according to the corresponding TMAH
20 concentration for reuse.

1 8. The method as claimed in claim 7, further
2 comprising the steps of:

3 diluting the recycled developer solution when the
4 absorption value $A1$ at the wavelength 210 nm
5 exceeds 1.2;

6 re-measuring absorptions of the diluted recycled
7 developer solution at wavelengths 210 nm and
8 220nm as $A1$ and $A2$.

1 9. A recycling system of a photoresist developer
2 solution containing tetra-methyl-ammonia hydroxide
3 (TMAH), comprising:

4 a recycle tank collecting the recycled developer
5 solution from a photoresist development system
6 via a recycle pipeline;

7 an adjustment tank loaded with highly concentrated
8 TMAH and connected to the recycle tank with an
9 adjustment pipeline;

a spectrometer for measuring absorption values of the developer solution in the recycle tank;
a processor connecting to the spectrometer and the adjustment pipeline, programmed to calculate a TMAH concentration in the recycle tank according to the measured absorption values from the spectrometer and delivering an amount of highly concentrated TMAH from the adjustment pipeline to the recycle tank to achieve a desired TMAH concentration according to the calculated TMAH concentration, wherein the processor is programmed to calculate the TMAH concentration in the recycle tank by the following steps:

reading absorption values Y_1 to Y_m on m wavelengths between 220 nm and 250 nm of the recycled developer solution respectively, wherein m is equal to or larger than 2, and an absorption value A_1 of 210 nm;

inputting the Y_1 to Y_m to an n th-degree polynomial to generate a wavelength-absorption relationship $Y = C_1X^n + \dots + C_{n-1}X + C_n$, wherein X is wavelength, n is a positive integer and C_1 to C_n are coefficients of the relation;

inputting wavelength 210 nm into the wavelength-absorption relationship to generate an absorption value Y_{210} ;

calculating a difference A_3 between the A_1 and Y_{210} as the absorption value of TMAH in the developer solution; and

40 inputting A3 to an absorption calibration curve of
41 TMAH at 210 nm to generate a corresponding TMAH
42 concentration in the recycle tank.

1 10. The recycling system as claimed in claim 9,
2 wherein the processor is a computer.

1 11. The recycling system as claimed in claim 9,
2 wherein the m wavelengths are selected with an interval
3 of 5 nm or 10 nm.

1 12. The recycling system as claimed in claim 11,
2 wherein the m wavelengths are the 7 wavelengths 220 nm,
3 225 nm, 230 nm, 235 nm, 240 nm, 245 nm and 250 nm.

1 13. The recycling system as claimed in claim 9,
2 wherein the nth-degree polynomial is a 2nd- to 5th-degree
3 polynomial.

1 14. The recycling system as claimed in claim 13,
2 wherein the nth-degree polynomial is a 3rd-degree
3 polynomial as in $Y=C_1X^3+C_2X^2+C_3X+C_4$.

1 15. The recycling system as claimed in claim 9,
2 further comprising a dilutor for diluting the recycled
3 developer solution when the absorption value A1 at the
4 wavelength 210 nm exceeds 1.2.

1 16. A recycling system of a photoresist developer
2 solution containing tetra-methyl-ammonia hydroxide
3 (TMAH), comprising:

4 a recycle tank collecting the recycled developer
5 solution from a photoresist development system
6 via a recycle pipeline;
7 an adjustment tank loaded with highly concentrated
8 TMAH and connected to the recycle tank with an
9 adjustment pipeline;
10 a spectrometer for measuring absorption values of
11 the developer solution in the recycle tank;
12 a processor connected to the spectrometer and the
13 adjustment pipeline, programmed to calculate a
14 TMAH concentration in the recycle tank
15 according to the measured absorption values
16 from the spectrometer and delivering an amount
17 of highly concentrated TMAH from the adjustment
18 pipeline to the recycle tank to achieve a
19 desired TMAH concentration according to the
20 calculated TMAH concentration, wherein the
21 processor is programmed to calculate the TMAH
22 concentration in the recycle tank by the
23 following steps:
24 reading absorption values A1 and A2 of the recycled
25 developer solution at wavelength 210 nm and 220
26 nm;
27 calculating an absorption value A3 of TMAH in the
28 developer solution by $A3 = A1 - A2 \times Co$, wherein Co
29 $= (A1' - A3') / A2'$, A1' and A2' are absorption
30 values of a recycled developer solution with
31 known TMAH concentration at wavelengths 210 nm
32 and 220 nm respectively, and A3' is the

33 standard absorption value of the known TMAH
34 concentration at 210 nm;
35 inputting A3 to an absorption calibration curve of
36 TMAH at 210 nm to generate a corresponding TMAH
37 concentration in the recycle tank.

1 17. The recycling system as claimed in claim 16,
2 wherein the processor is a computer.

1 18. The recycling system as claimed in claim 16,
2 further comprising a dilutor for diluting the recycled
3 developer solution when the absorption value A1 at the
4 wavelength 210 nm exceeds 1.2.